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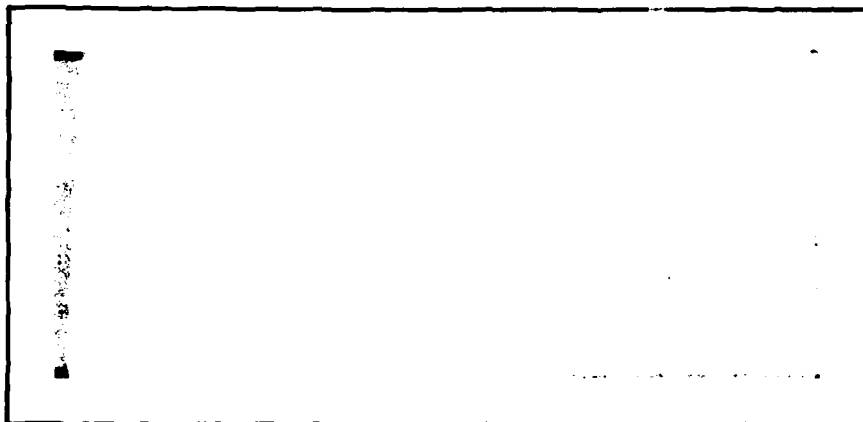
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AFOSR CONTRACT F49620-78-C0050  
ATMOSPHERIC TRIATOMIC MOLECULAR STUDIES  
NOVEMBER 17, 1980

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A systematic study at the SCF and MCSCFCI level has been made of several of the fifteen triatomic atmospheric molecules which have formed the focus on this and previous work. In addition a powerful new (MCSCF) method has been developed and partially implemented. Also, in order to achieve accurate electron affinities and ionization potentials, a new scheme for configuration selection has been developed called the differential correlation energy method. This method has been tested on the processes, $\text{CH}+\text{CH}^+$ and $\text{CO}_2^+ + \text{CO}_2$ .			

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## I. Introduction and Objectives

The purpose of this report is to present work performed under this AFOSR contract. As has been repeatedly discussed elsewhere (Ref. 1-5) the thrust of this project is triple pronged: 1) to calculate on a consistent and comprehensive basis basic energy quantities for the triatomic molecules  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{O}_3$  and their positive and negative ions. These quantities include the vertical spectra, the ionization potentials and the electron affinities of these systems. As part of this effort portions of potential energy surfaces are computed and used to predict vibrational spectra and to interpret the mechanisms of chemical reactions of interest. 2) second the development of two new methods for treating electronic structures will be discussed. 3) the third topical area of this research involves the study of specific atmospheric problems involving these molecular systems as they are brought to our attention through the literature or directly by experimentalists. In this section a molecule by molecule summary will be given.

This report will follow the above structure. First, overall status will be given, then progress on two new method development projects (MCSCF and Differential Correlation Energy (DCE) will be summarized, next a molecule by molecule summary summary will be given.

## II. Overall Status of Molecular Project

The overall status of the triatomic project is summarized in Table I. This is a cumulative table with results obtained during the current contract period (March 1, 1978 - May 30, 1980), given in parenthesis.

Reference to papers published covering work in Table I are given in Appendix I.

TABLE I

ELECTRONIC STATES TO WHICH ATTENTION HAS BEEN THUS FAR GIVEN  
IN THE THEORETICAL AIR TRIATOMICS PROJECT AND ASSOCIATED THEORETICAL PROJECTS<sup>a,b</sup>

System	Vertical Electronic Spectrum <sup>c</sup>		Surface Scans	Comments <sup>d</sup> Surface-Cuts	Vibrational Spectra
	SCF	Correlated			
$H_2O^+$	$2B_1(2), A_1(2), B_2(2), A_2$ $4B_1, A_2, B_2(2)$	$2B_1, B_2, A_1, A_2$ $4B_1, A_1$	$X^2B_1, B_2$	$R_1, R_2, \theta$	$X^2B_1, B_2$
$H_2O$	$1, 3A_1, B_1, A_2, B_2$	$1A_1, 3B_1$	$X^1A_1$ $3B_1$	$R_1, R_2$ $R_1, R_2; \theta$	
$H_2O^-$					
$N_2O^+$	$2\pi(4), \Sigma^\pm(2), \Delta(2), \Phi$ $4\pi(3), \Sigma^\pm(2), \Delta(2)$ $1A'(2), 1A''(2), 4A', 4A''$	$2\pi(2), \Sigma^\pm, \Delta$ $4\pi, \Sigma^\pm, \Delta$	$[X^2\pi, \Sigma^+, A'']$ $1^4\Sigma^-, 2^4\Sigma^-,$ $a^4A''$	$R_1, R_2, \theta$ $R_1, R_2, \theta$	$1^4\Sigma^-$ $X^2\pi_+$ $A^2\Sigma^+$ $a^4A''$
$N_2O$	$1\Sigma^+(3), \Sigma^-, \pi(2), \Delta$ $3\Sigma^+(2), \Sigma^-, \pi(2), \Delta$ $5\Sigma^+, 5\pi$ $1A'(2), 1A'', 3A', 3A''$	$1\Sigma^+(2), \Sigma^-, \pi(2), \Delta$ $3\Sigma^+, \Sigma^-, \pi(2), \Delta$ $5\Sigma^+$	$1^+\Sigma^-, \Sigma^-, \pi, \Delta$ $3^+\Sigma^-, \Sigma^-, \pi, \Delta$ $1A', A''$ $3A', A''$	$R_1, R_2; \theta$ $R_1, R_2; \theta$	$X^1\Sigma^+$



TABLE I (con't.)

System	Vertical Electronic Spectrum <sup>c</sup>		Surface Scans	Comments Surface-Cuts	Vibrational Spectra
	SCF	Correlated			
$N_2O^+$	$2\Pi(2), \Sigma^+(3), \Sigma^-(2), \Delta(2), \Phi$ $4\Pi(2), \Sigma^+, \Sigma^-(2), \Delta$ $6\Sigma^+$ $2A'(2), 2A''(2), 4A''(2)$	$2\Pi, \Sigma^+$ $4\Sigma^+, \Sigma^-, \Delta$	$X^2A'$	$R_1, R_2, \theta$	$X^2A'$
$CO_2^+$	$2\Pi_g, \Pi_u(2), \Sigma_u^+, \Sigma_g^+$ $4\Pi_u$ $2B_2(2), A_2, B_1(2), A_1(3)$ $4B_1, A_1$	$2\Pi_g, \Pi_u(2), \Sigma_u^+, \Sigma_g^+$ $4\Pi_u$			
$CO_2$	$[1\Sigma_g^+(5)], 3\Sigma_g^+(4)$ $1, 3\Sigma_g^-(2), \Sigma_u^-(4), [\Sigma_u^-(2), 3\Sigma_u^+]$ $1, 3\Pi_g(5), \Pi_u(5), \Delta_g(3), [\Delta_u(3)]$ $1, 3\Phi_g, \Phi_u$ $1A_1, A_2(2), B_2(2)$ $3B_2(2), A_2(2)$	$1\Sigma_g^+, \Sigma_u^-, \Delta_u$ $3\Sigma_u^+, \Delta_u$	$[X^1\Sigma_g^+(^1A_1)]$	$R, \theta$	

TABLE I (con't.)

System	Vertical Electronic Spectrum <sup>c</sup>		Surface Scans	Comments Surface-Cuts	Vibrational Spectra
	SCF	Correlated			
$\text{CO}_2^-$	$2\pi_u, \Sigma_g^+, \Sigma_u^+, \Phi_g$ $4\pi_g$ $[2A_1(2), B_1, B_2(3), A_2(2)]$	$2\pi_u, \Sigma_g^+, \Sigma_u^+, \Phi_g, \pi_g$ $4\pi_g$ $[X^2A_1]$	$[X^2A_1]$	R, $\theta$	
$\text{NO}_2^+$	$1A_1, A_2, B_2, B_1$ $3B_2, A_2, A_1, B_1$ $1\Sigma_g^+, \Sigma_u^+(2), \pi_u, \pi_g(2), \Delta_u, \Delta_g$ $3\Sigma_g^+, \Sigma_u^+(2), \pi_u, \pi_g(2), \Delta_u, \Delta_g$	$1A_1, A_2, B_2, B_1$ $3A_1, A_2, B_2, B_1$ $X^1\Sigma_g^+, \Delta_g, \Sigma_g^-, \pi_g(2)$ $1\Sigma_u^+, \Delta_u, \pi_u(2)$ $3\Sigma_g^+, \Delta_g, \pi_g(2)$ $3\Sigma_u^+, \Delta_u, \pi_u$	$X^1\Sigma_g^+, ^1A'$	$R_1, R_2, \theta$	$X^1\Sigma_g^+(A')$
$\text{NO}_2$	$[2A_1(2), B_1, A_2(4), B_2(4)]$ $4B_2, A_2$	$2A_1, B_1, B_2, A_2$ $4B_2, A_2$ $2\Sigma_g^+$	$X^2A_1, B_2, B_1, A_2$ $4A_2, B_2$ $2\Sigma_g^+$	R, $\theta$  $R_1, R_2$	
$\text{NO}_2^-$	$[1A_1, B_1, A_2, B_2]$ $3B_1, B_2, [A_2], A_1$		$[X^1A_1]$ $[1^1A']$	R, $\theta$ $R_1, R_2, \theta$	

TABLE I (con't.)

System	Vertical Electronic Spectrum <sup>c</sup>		Surface Scans	Comments Surface-Cuts	Vibrational Spectra
	SCF	Correlated			
$O_3^+$	$^2A_2(2), A_1(2), B_2(2), B_1(2)$ $^4A_2, B_2; A_1, B_1$	$^2A_1, A_2, B_1, B_2$ $^4A_1, A_2, B_1, B_2$	$X^2A_1$	$\theta$	
$O_3$	$^1A_1(2), A_2(2), B_2(2), B_1$ $^3B_2(2), B_1(2), A_2(2), A_1$	$^1A_1, A_2, B_2, B_1$ $^3B_2, B_1, A_2, A_1$ $^1A_1''$	$X^1A_1$ $a^3B_1$	$R_1, R_2, \theta$ $R_1, R_2, \theta$	$X^1A_1$ $a^3B_1$
$O_3^-$	$^2B_1, A_1, B_2, A_2$ $^4B_2(2), A_2(2), B_1(2), A_1(2)$	$^2B_1, A_1, A_2, B_2$ $^4B_1, A_1, A_2, B_2$	$X^2B_1$	$\theta$	

<sup>a</sup>These calculations have been performed with a double-zeta or better quality basis set. Most of the correlated vertical excitations have now also been performed with basis sets augmented with polarization and, where needed, diffuse functions. Correlation is at the MCSCF/CI optimized valence level.

<sup>b</sup>Properties such as the dipole moment are available for most SCF and all correlated wavefunctions of each molecule-state reported in this table. The dipole moment function is available for the correlated geometry scans.

<sup>c</sup>Some adiabatic excitation energies have been obtained for  $H_2O^+$ ,  $H_2O$ ,  $N_2O^+$ ,  $N_2O$ ,  $N_2O^-$ ,  $NO_2^+$ ,  $NO_2$ , and  $O_3$ .

TABLE I FOOTNOTES (CONT'D)

- d.  $R_1, R_2, \theta$  Indicates portions of the energy surface in which all three geometry parameters have been varied have been done.
- $R_1, R_2$  Indicates only bond lengths have been varied at fixed angle.
- $R, \theta$  Symmetric bond variation and angular variation.
- $\theta$  Only angle variation explored.

### III. The Differential Correlation Energy Method

#### a. Introduction

Although potential curves of chemical accuracy can now be computed routinely, the calculation of electron affinities and ionization potentials still presents a considerable challenge. Methods which have been used to calculate electron affinities and ionization potentials are extensive configuration interaction, equations of motion, pair energy schemes, Hess cycles, perturbation theory, Koopmans theorem and Hartree Fock methods.

The Hartree-Fock model (and Koopman's theorem) usually yield electron affinities and ionization potentials which are in error by several eV, however through fortuitous cancelation of basis set and correlation errors, good agreement with experiment is sometimes obtained. The errors in other methods are usually smaller however only extensive configuration interaction or Hess cycle calculations have yielded quantitative results.

In this section we present a configuration selection scheme designed to only include those excitations which directly contribute to the correlation energy difference between the neutral and ionic system. The orbitals for each configuration are evaluated via the MCSCF method. We call this scheme the Differential Correlation Energy (DCE) method.

#### b. The Differential Correlation Energy Method

We are currently developing a new method for choosing configurations in a MCSCF/CI calculation to give accurate (within 0.1 eV) electron affinities and ionization potentials using the smallest number of configurations possible. The key to this method is the determination of the configurations which contribute to the differential correlation energy (DCE) associated with the addition or removal of an electron. It is our aim to develop a prescription for the choice DCE configurations analogous to the OVC prescription<sup>6</sup> for the choice of configurations to give accurate ( $\pm .1$  eV) bond dissociation energies. THE OVC method concentrates only on the changes in correlation energy associated with bond formation.

The DCE method takes advantage of some simple properties of correlation energy,

- 1) Correlation energy is very sensitive to electron occupations, i.e., new pairs, orbital occupations.
- 2) Correlation energy is relatively insensitive to details of orbital shapes.
- 3) Pair energy schemes work.

In light of the above.

- 1) It is reasonable to evaluate only the correlation energy difference between neutrals and ions or different states.
- 2) Major differences come from new pairs formed and cross shell correlation of extra electrons with remaining ones. (Active orbital contribution).
- 3) Minor differences some from pair correlation energy contribution due to availability of open orbital. (Excluded space effect.)

c. Formal Development for Electron Affinities and Ionization Potentials

Below we give specifically the formulation of ideas proposed for the calculation of electron affinities by the DCE method.

In order to discuss electron affinity or ionization potential, it is convenient to use a second-quantized treatment. Thus we introduce the usual electron annihilation and creation operators  $a_i$  and  $a_i^+$ , respectively. The index  $i$  serves to distinguish among different spin-orbitals in our ordered base. The operators satisfy the anticommutation relations

$$\{a_i, a_j\} = \{a_i^+, a_j^+\} = 0 ,$$

$$\{a_j^+, a_j\} = \delta_{ij} .$$

Now if  $\phi$  denotes an electronic state function (in Fock space),  $a_i^+ \phi$  will describe the same state function with an additional electron in the  $i$ -th orbital. This assumes that the  $i$ -th orbital is unoccupied in  $\phi$ . For simplicity, we shall assume that  $\phi$ , and consequently  $a_i^+ \phi$ , represent single-configuration state functions.

The Hamiltonian can be written

$$H = \sum_{ij} a_i^\dagger h_{ij} a_j + \frac{1}{2} \sum_{ij} \sum_{kl} a_i^\dagger a_k^\dagger g_{ij,kl} a_l a_j$$

This can be partitioned according to

$$H = H_0 + H',$$

where

$$H_0 = \sum_{ij} a_i^\dagger h_{ij}^0 a_j,$$

$$H' = \sum_{ij} a_i^\dagger (h_{ij} - h_{ij}^0) a_j + \frac{1}{2} \sum_{ij} \sum_{kl} a_i^\dagger a_k^\dagger g_{ij,kl} a_l a_j.$$

We have not specified our orbital base in detail, so we are free to assume that it is chosen so that

$$h_{ij}^0 = \delta_{ij} \epsilon_i.$$

Then  $\phi$  and  $a_i^\dagger \phi$  are eigenvectors of  $H_0$ ; that is,

$$H_0 \phi = E_0 \phi,$$

$$H_0 a_i^\dagger \phi = (E_0 + \epsilon_i) \phi,$$

where

$$E_0 = \sum_{i \in \phi} \epsilon_i.$$

We have some freedom in the choice of  $h^0$ ; for example, we can choose  $h^0$  so as to give Hartree-Fock orbitals (for the state  $\phi$ ) as its eigenfunctions. Note that in this case  $E_0$  is not the Hartree-Fock energy for the state; the Hartree-Fock energy is given by  $\langle \phi | H | \phi \rangle$ .

No matter what the choice of  $h^0$  we use,  $\phi$  will not be an eigenvector of  $H$  because of electron correlation effects, and the same observation applies also to  $a_i^\dagger \phi$ . We can compute these correlation effects approximately by application of Rayleigh-Schrodinger perturbation theory, with  $H_0$  as the unperturbed Hamiltonian and  $H'$  as the perturbation.

This yields to first order,

$$\Psi = \phi + R\phi ,$$

$$\Psi_e = a_i^+ \phi + R a_i^+ \phi ,$$

where

$$R = \sum_{ij, i \neq j} a_i^+ (h_{ij} - h_{ij}^0) a_j / (\epsilon_j - \epsilon_i) \\ + \frac{1}{2} \sum_{ij} \sum_{kl, \epsilon_i + \epsilon_k \neq \epsilon_j + \epsilon_l} a_i^+ a_k^+ g_{ij,kl} a_l a_j / (\epsilon_l + \epsilon_j - \epsilon_i - \epsilon_k) .$$

To second order the energies are given by

$$E = \langle \phi | H | \phi \rangle + \langle \phi | H' R | \phi \rangle ,$$

$$E_e = \langle \phi | a_i H a_i^+ | \phi \rangle + \langle \phi | a_i H' R a_i^+ | \phi \rangle .$$

Since we have  $a_i a_i^+ \phi = \phi$ , the electron affinity is given to second order by

$$E_e - E = \epsilon_i + \langle \phi | [a_i, H'] a_i^+ | \phi \rangle \\ + \langle \phi | [a_i, H'] R a_i^+ + H' [a_i, R] a_i^+ | \phi \rangle .$$

From this expression we see that the computed electron affinity remains unaltered to this order if we modify  $H'$  by adding to it any Hermitian operator that commutes with  $a_i$ . Hence we can use in place of  $H'$  the expression

$$H'' = a_i^+ H'_+ + H'_- a_i$$

where

$$H'_+ = \sum_j \left[ h_{ij} - h_{ij}^0 + \sum_k a_k^+ a_l g_{ij,kl} \right] a_j , \\ H'_- = \sum_j a_j^+ \left[ h_{ji} - h_{ji}^0 + \sum_{kl} a_k^+ a_l g_{ji,kl} \right] .$$



In other words, any part of  $H''$  that does not reference the orbital  $i$  does not contribute to the computation of the electron affinity.

It is not advisable to take the above argument too literally. For example, it does not indicate that many-body perturbation theory will give a good result for the electron affinity if carried to second order only. Higher order effects are likely to prove important. Many of these effects are automatically included in a SCF or MCSCF treatment, so we shall not pursue such questions further. What remains is a guide in attempting to answer the question: What configurations are needed to handle electron correlation effects that directly affect the calculation of electron affinity? From the above discussion, the configuration lists

$$\Phi, a_i^+ a_j^+ a_k a_l \Phi, \text{ any } j, k, l, \neq i,$$

$$a_i^+ \Phi, a_j^+ a_k^+ a_l \Phi, \text{ any } j, k, l, \neq i,$$

appear as the answer to this question. In essence, this tells us that for the state without the added electron we should include the dominant (i.e., Hartree-Fock) configuration and all single and double replacements which contain the orbital of the electron to be added. For double replacements, we note that in addition to the spin orbital  $i$ , the configuration may also contain another orbital from this shell. For the state with the added electron, we should again include the dominant configuration and any single and double replacements that are generated by eliminating the spin orbital of the added electron in the dominant configuration.

Some obvious refinements can be added to this scheme: single replacements from the dominant configuration are unlikely to be important, since Brillouin's theorem applies to an SCF approach, and replacements which involve excitation of a core orbital are probably negligible because a large excitation energy is involved (the core orbitals can be defined as those orbitals to which such an argument applies). We also must be concerned with the need for a multiconfiguration reference state.

A similar analysis is being performed for the calculation of vertical spectra.

d. Applications

Using the DCE configuration selection rules MCSCF calculations have been performed on  $\text{CN} \rightarrow \text{CN}^-$  and  $\text{CO}_2^- \rightarrow \text{CO}_2$ .

For  $\text{CN}^-$  we must include all correlation within the  $5\sigma^2$  orbital and all cross shell correlation of  $5\sigma^2$  with  $3\sigma^2$ ,  $4\sigma^2$ , and  $1\pi$ . Using 3 new MCSCF correlating orbitals,  $6\sigma$ ,  $7\sigma$ ,  $2\pi$  this yields 25 configurations.

For CN the DCE perscription tells us to include all cross shell correlation involving the  $5\sigma$  orbital and all excitations into the half filled  $5\sigma$  orbital. This yields 41 configurations. Results of these calculations are presented in Table II.

For  $\text{CO}_2$  we must include all valence excitations into the  $6a_1$  orbital, this yields 67 configurations. For  $\text{CO}_2^-$  we must include all cross shell correlation of  $6a_1$  electron with valence shell and valence excitations into  $6a_1$  orbital. Results on  $\text{CO}_2^- \rightarrow \text{CO}_2$  are presented in Table III.

These results indicate that the DCE rules may provide a reasonable starting point for the MCSCF procedure which can then be followed by a larger CI for truly quantitative results.

TABLE II  
DCE METHOD APPLIED TO CN CN<sup>-</sup>

<u>State/Energy</u>	<u>MCSCF/CI 15/26</u>	<u>Single/Conf.</u>	<u>SCF</u>	<u>ΔE</u>
CN <sup>-</sup> R=2.117	-92.3724551	-92.321633	-92.3221717	.0508
" 2.217	-92.3812117	-92.326182	-92.3267819	.0550
" 2.317	-92.3780383	-92.318317	-92.3189866	.0597
CN(19MC)2.117	not converged		-92.2045157	
" 2.217	" "		-92.2027169	
" 2.317	-92.2510795	-92.172356	-92.1890972	.0787
CN(fromCN <sup>-</sup> ) 2.117	-91.9523405	-91.905750	-92.2045157	.0466
2.217	-91.9451404	-91.897083	-92.2027169	.0491
2.317	-91.9445647	-91.895993	-92.2090972	.0486
CN(17MC)2.117	-92.2317141	-92.203380	-92.203380	.0312
2.217	-92.2402757	-92.201029	-92.2027169	.0392
2.317	-92.2358326	-92.186712	-92.1890972	.0491

TABLE III

DCE

METHOD

APPLICATION TO  $\text{CO}_2^- \rightarrow \text{CO}_2$  $(\theta_{\text{OCO}} = 135.77^\circ, R_{\text{CO}} = 2.3734 \text{ bohrs})$ Configurations for  $\text{CO}_2^-$ 

Orbitals

1a <sub>1</sub>	1b <sub>2</sub>	2a <sub>1</sub>	3a <sub>1</sub>	4b <sub>2</sub>	4a <sub>1</sub>	2b <sub>2</sub>	5a <sub>1</sub>	3b <sub>2</sub>	6a <sub>1</sub>	7a <sub>1</sub>	5b <sub>2</sub>	1b <sub>1</sub>	1a <sub>2</sub>	2b <sub>1</sub>
2	2	2	2	2	2	2	2	2	1	0	0	2	2	0

- 1) Include all cross shell correlation of 6a<sub>1</sub> electron with valence electrons.
- 2) Include all valence excitations into 6a<sub>1</sub> orbital.

E = -187.56976 a.u.      19MCSCF/70CI

Configurations for  $\text{CO}_2$ 

2	2	2	2	2	2	2	2	2	0	0	0	2	2	0
---	---	---	---	---	---	---	---	---	---	---	---	---	---	---

- 1) Include all valence excitations into 6a<sub>1</sub> orbital

E = -187.52993 a.u.      19MCSCF/67CI

 $\Delta E = 1.08 \text{ ev}$  $\Delta E = .3 \text{ ev}$  (basis set error in  $\text{CO}_2^-$ )Vertical Ionization Potential of  $\text{CO}_2^- \sim 1.4 \text{ ev}$ Experimental\* IP of  $\text{CO}_2^-$        $1.4 \pm .3 \text{ ev}$

#### IV. A Multidimensional Newton-Raphson MCSCF Method

The merits of the MCSCF approach to the calculation of electronic wave functions for atoms or molecules are well documented<sup>6</sup> and, in fact, the method has become the standard starting point for most researchers. The principal limitation of this approach has been the frequent difficulty in obtaining converged solutions for the MCSCF wave function. A new MCSCF method<sup>7</sup> under development by J. Detrich and C.C.J. Roothaan\* is expected to eliminate this difficulty.

This method applies whenever the spin-orbitals (SO) are put forward as finite expansions in terms of a basis set. In the MCSCF approach one also constructs term state functions (TSF) as linear combinations of configuration state functions (CSF); the latter are defined as symmetry-adapted linear combinations of Slater determinants arising from a single configuration of orbital assignments. A complete set of trial SO's can be put forward, which spans the same linear space as the one-electron basis functions, and, analogously a set of trial TSF's spanning the same linear space as the set of CSF's can be developed.

The method deals in terms of the unitary transformations of the reference SO's and TSF's which will give optimized SO's and TSF's. These unitary transformations are expressed as exponentials of anti-Hermitian operators. In terms of the reference SO's and TSF's, the variational energy expression is of the form

$$E' = E + \sum_i E_i x_i + \frac{1}{2} \sum_{ij} E_{ij} x_i x_j + \dots,$$

where the  $x_i$ 's are the independent matrix elements of the anti-Hermitian operators. The quantities  $E$ ,  $E_i$  and  $E_{ij}$  are evaluated by rather elaborate contractions involving integrals over basis functions, occupation numbers and coupling constants, and the expansion coefficients representing the set of reference SO's and TSF's.

Approximating this expression by dropping all terms of third and higher order, the extremum of  $E'$  with respect to all the variables  $x_i$  occurs when they satisfy

$$\sum_j E_{ij} x_j = -E_i$$

Once the solution of this equation has been obtained, new reference SO's and TSF's are easily computed, thus completing an iterative MCSCF cycle.

This method is seen to be a multidimensional generalization of the Newton-Raphson iterative process, and it converges quadratically in the general case. The availability of such a method will substantially enhance the range of problems where the advantages of the MCSCF approach can be exploited. Even in cases where other MCSCF methods suffice, the availability of a method that virtually guarantees convergence in a few iterations is expected to significantly reduce the man-hours required to perform a given series of calculations. These advantages indicate that the new method will become the standard vehicle for molecular orbital calculations in the basis-set expansion regime.

A preliminary implementation of this method has been coded for atoms under the auspices of the National Resource for Computation in Chemistry by Prof. Roothaan. A comprehensive description of the formalism and analysis for the method is currently in preparation.

\*Professor C. C. J. Roothaan is a technical consultant on self consistent field techniques to SAI.

## V. Molecule by Molecule Summary

### CO<sub>2</sub> and its Ions

Work on CO<sub>2</sub> and its ions during the contract period consisted primarily of trial calculations intended to help establish an efficient and reliable approach to the calculation of electron affinities and ionization potentials. As discussed in Section III above, this goal has motivated development of the Differential Correlation Energy (DCE) method. The calculations for CO<sub>2</sub> and CO<sub>2</sub><sup>-</sup> summarized here serve as a test for the method.

For both CO<sub>2</sub> and CO<sub>2</sub><sup>-</sup> the (3s,2p) contracted Cartesian Gaussian basis of Dunning<sup>8</sup> was adopted. This choice permits trial calculations to be economically performed, but involves some sacrifice in accuracy of the orbital description. As an aid in assessing such effects, SCF vertical spectra for CO<sub>2</sub> were computed with the (3s, 2p) basis and compared with previous results using a more flexible basis<sup>9</sup> at the experimental linear equilibrium geometry (Table IV) and a bent geometry (Table V). In general, the SCF vertical spectra for CO<sub>2</sub> are in good agreement, the only exception being in the case of the  $1\Sigma_u^+$  state, which is predominantly Rydberg rather than valence in character,<sup>10</sup> and hence not well described by a basis set which does not contain diffuse functions. This indicates that the correlation effects of interest are reasonably well described in terms of the (3s, 2p) basis. Another indication of the utility of the (3s, 2p) basis comes from the results of an SCF geometry scan for the ground state of CO<sub>2</sub><sup>-</sup>. The equilibrium geometry is found to be  $\theta_{OCO} = 136^\circ$ ,  $R_{CO} = 2.37$  bohr, in good agreement with the determination  $\theta_{OCO} = 135^\circ$ ,  $R_{CO} = 2.35$  bohr by Pacansky, Wahlgren and Bagus<sup>11</sup> using a considerably larger basis.

The DCE method was applied to compute the vertical ionization potential of CO<sub>2</sub><sup>-</sup> at the SCF equilibrium geometry  $\theta_{OCO} = 135.77^\circ$ ,  $R_{CO} = 2.3734$  bohrs. In addition to the orbitals occupied in the dominant ground state CO<sub>2</sub><sup>-</sup> configuration, three correlation orbitals,  $7a_1$ ,  $5b_2$ ,  $2b_1$ , were introduced. The list of configurations developed according to the DCE method contained

70 for  $\text{CO}_2^-$  and 67 for  $\text{CO}_2$ . The orbitals were taken from an MCSCF calculation for  $\text{CO}_2^-$  involving the 19 most significant configurations from the list of 70 DCE configurations for  $\text{CO}_2^-$ . Note that the orbitals from  $\text{CO}_2^-$  calculation were used in the  $\text{CO}_2$  as well; this was the only obvious way to preserve the character of the  $6a_1$  orbital in the  $\text{CO}_2$  calculation.

The energy computed from the 67-configuration interaction calculation for  $\text{CO}_2$  was  $E = 187.52993$  hartrees; from the 70-configuration interaction calculation for  $\text{CO}_2^-$  the energy  $E = -187.56976$  was obtained. This implies a vertical ionization potential for  $\text{CO}_2^-$   $\Delta E = 1.08$  eV.

As noted above, the basis set adopted affects the accuracy of this result. Since the effect is not expected to depend strongly on correlation, one can obtain a quantitative estimate by comparing the SCF result for the  $\text{CO}_2$  adiabatic electron affinity computed with the (3s,2p) basis,  $-.65$  eV, with the corresponding SCF result from Pacansky, *et.al.*,<sup>11</sup>  $-.38$  eV. This indicates a basis set error of about  $.3$  eV. Revising our computed result accordingly gives  $1.4$  eV for the vertical ionization potential of  $\text{CO}_2^-$ .

Strictly speaking, there is no corresponding experimental determination, but a close analogue can be constructed as follows. When  $\text{CO}_2$  is distorted from its experimental equilibrium geometry to the theoretical  $\text{CO}_2^-$  equilibrium geometry adopted in these calculations, the  $\text{CO}_2$  potential constructed by Suzuki<sup>12</sup> from spectroscopic data gives a distortion energy of  $2.0$  eV.

Adding this to the experimentally derived  $\text{CO}_2$  electron affinity of  $-.6 \pm .2$  eV reported by Compton, Reinhardt and Cooper<sup>13</sup> yields  $1.4 \pm 0.3$  eV for the  $\text{CO}_2^-$  vertical ionization potential.

This result is in good agreement with the result based on the DCE method.



More refined computations are necessary to confirm our estimate of basis set error, but our present results already establish the DCE method as a promising new approach.

TABLE IV  
LINEAR CO<sub>2</sub> VERTICAL SPECTRUM

$$r_1=r_2 = 2.1944 \text{ bohrs } \theta = 180^\circ$$

State	Configuration(s) <sup>a</sup>						Energy		4s,3p Energy <sup>c</sup> eV <sup>b</sup>
	1 $\pi_{ux}$	1 $\pi_{gx}$	2 $\pi_{ux}$	1 $\pi_{gy}$	1 $\pi_{uy}$	2 $\pi_{gy}$	a.u.	eV <sup>b</sup>	
$\chi^1\Sigma_g^+$	2	2	0	2	2	0	-187.553005	0.00	0.00
$^3\Sigma_u^+$	{	2	0	2	1	1	-187.292459	7.09	7.07
		2	1	2	2	0			
$^3\Sigma_u^-$	{	2	0	2	1	1	-187.270395	7.69	7.66
		2	1	2	2	0			
$^3\Sigma_u^-$	{	2	1	2	1	0	-187.270654	7.68	—
		2	1	2	2	1			
$^3\Sigma_u^-$	{	2	1	2	1	0	-187.249106	8.27	8.26
		2	1	2	2	1			
$^1\Sigma_u^-$	{	2	1	2	1	0	-187.249361	8.26	8.26
		2	1	2	2	1			
$^1\Delta_u$	{	2	1	2	1	0	-187.238979	8.54	—
		2	1	2	2	1			
$^1\Delta_u$	{	2	0	2	1	1	-187.279319	7.45	8.52
		2	1	2	2	0			
$^1\Sigma_u^+$	{	2	0	2	1	1	-186.901777	17.72	14.15
		2	1	2	2	0			

$$^a \text{Core} = 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 3\sigma_g^2 2\sigma_u^2 4\sigma_g^2 3\sigma_u^2$$

$$^b 1 \text{ a.u.} = 27.21070 \text{ eV}$$

<sup>c</sup>From reference 9.

TABLE V  
BENT CO<sub>2</sub> VERTICAL SPECTRUM

[3s,2p] Basis, SCF

$r_1=r_2= 2.1944$  bohrs  $\theta=130^\circ$

State	Configuration <sup>a</sup>						Energy		4s/3p Energy <sup>c</sup> eV <sup>b</sup>
	5a <sub>1</sub>	4b <sub>2</sub>	6a <sub>1</sub>	1b <sub>1</sub>	1a <sub>2</sub>	2b <sub>1</sub>	a.u.	eV <sup>b</sup>	
1 <sup>1</sup> A <sub>1</sub>	2	2	0	2	2	0	-187.462871	0.00	0.00
1 <sup>3</sup> B <sub>2</sub>	2	1	1	2	2	0	-187.394377	1.86	2.00
1 <sup>3</sup> A <sub>2</sub>	2	2	1	2	1	0	-187.363691	2.70	2.76
1 <sup>1</sup> A <sub>2</sub>	2	2	1	2	1	0	-187.352623	3.00	3.07
1 <sup>1</sup> B <sub>2</sub>	2	1	1	2	2	0	-187.316653	3.98	4.05
2 <sup>3</sup> B <sub>2</sub>	2	2	0	2	1	1	-187.239182	6.09	6.13
2 <sup>3</sup> A <sub>2</sub>	2	1	0	2	2	1	-187.220412	6.60	6.70
2 <sup>1</sup> A <sub>2</sub>	2	1	0	2	2	1	-187.208979	6.91	7.01
2 <sup>1</sup> B <sub>2</sub>	2	2	0	2	1	1	-187.080537	10.40	10.39

<sup>a</sup>Core= 1a<sub>1</sub><sup>2</sup>1b<sub>2</sub><sup>2</sup>2a<sub>1</sub><sup>2</sup>3a<sub>1</sub><sup>2</sup>2b<sub>2</sub><sup>2</sup>4a<sub>1</sub><sup>2</sup>4b<sub>2</sub><sup>2</sup>

<sup>b</sup>1a.u. = 27.21070

<sup>c</sup>Reference 9

### $N_2O^+ X^2_{II}$ MCSCF/CI Calculation

A geometry scan for the equilibrium bond lengths of the linear  $N_2O^+ X^2_{II}$  state was performed. The wave functions were constructed from orbitals expanded in terms of a basis set consisting of a 4s,3p 1d Gaussian basis on each center. The MCSCF calculations consist of 20 configurations, and the supplementary CI calculations consist of 99 configurations.

The results for the linear NNO geometry indicate equilibrium bond lengths  $R_{NN} = 2.126$  a.u.,  $R_{NO} = 2.367$  a.u. A preliminary fit to a molecular potential function of the form

$$v = \frac{1}{2} K_{NN} (\Delta R_{NN})^2 + \frac{1}{2} K_{NO} (\Delta R_{NO})^2$$

yields  $K_{NN} = 19.563$  md/A<sup>0</sup>,  $K_{NO} = 5.144$  md/A<sup>0</sup>

A more elaborate characterization of the potential surface is needed in order to extract spectroscopic characteristics such as vibrational behavior.

### $NO_2^-$ Ground State Geometry Scan

A preliminary SCF-level geometry scan of the  $NO_2^-$  ground electronic state has been performed. They include the normal  $X^1A_1 C_{2v}$  state of equilibrium geometry, the peroxy well, and the energy-minimum pathway between the two geometries. As indicated in Table VI, the geometries of the  $C_{2v}$  and peroxy  $C_s$  minima are in good agreement with the earlier results of Pearson, et. al.<sup>14</sup> Hence the delineation of the potential surface between these two geometries is useful, although somewhat crude. It would appear that the indicated saddle point between the two geometries (Table VI) is above the molecular dissociation threshold, so that isomerization cannot be expected to take place. Evidently this is consistent with the experimental observations that bear on the existence of a  $NO_2^-$  peroxy well. On the other hand, a preliminary calculation cannot be relied upon with regard to such questions, and a more elaborate set of calculations utilizing multiple configurations and a larger basis set is planned.

TABLE VI  
PRELIMINARY SURVEY OF THE NO<sub>2</sub> X<sup>1</sup>A<sub>1</sub> (<sup>1</sup>A') HYPERSURFACE

SCF, (9s5p)/ [3s2p]<sup>a</sup>

Critical Geometry	E <sub>T</sub> + 203 (a.u.)	V (eV)	R <sub>NO</sub> (A)	R <sub>OO</sub> (A)	A <sub>ONO</sub> (deg.)	A <sub>OON</sub> (deg.)
C <sub>2v</sub>	-1.0247 (-1.0336)	0.0 (0.0)	1.27 (1.26)	2.17	116.8 (117.0)	31.
S.P. Ring	-0.83 (-0.8736)	5.3 (4.4)	2.28 (1.50)	2.06	63.8 (58.5)	82.6
C <sub>s</sub>	-0.9067 (-0.9161)	3.2 (3.2)	1.25 (1.25)	1.51 (1.49)	34.	118.2 (118.5)
D(ON-O <sup>-</sup> )		4.0				

<sup>a</sup>The values in parenthesis are (9s5p)/ [5s3p] results from reference 14.

The wave functions utilized in this set of calculations are based on the (3s,2p) contracted gaussian basis sets of Dunning.<sup>8</sup> In support of these calculations, the  $X^2A_1$ ,  $1^2A_1$ ,  $1^2B_1$ ,  $1^2B_2$ ,  $1^4B_2$ , and  $1^4A_2$  states of  $NO_2$  were computed using the same basis set. In Table VII these results are compared with earlier results<sup>9</sup> using the more elaborate 4s,3p basis set.

Similar calculations were performed for the  $1^3B_2$ ,  $1^1B_2$  and  $1^3A_1$  states of  $NO_2^-$ , as well as the  $X^1A_1$  ground state. These are of some interest in their own right, since they use the computed ground state  $NO_2^-$  equilibrium geometry, rather than the  $NO_2$  equilibrium geometry used previously,<sup>10</sup> or the experimental geometry adopted by Benioff<sup>15</sup>. Our results for the computed excitation energies are given in Table VIII. Our  $X^1A_1 \rightarrow 1^1B_2$  excitation energy appears to be in better agreement with experiment than obtained in previous work,<sup>8,13</sup> but more elaborate calculations are required to clarify whether this agreement is fortuitous.

TABLE VII  
COMPUTED SCF ENERGIES FOR NO<sub>2</sub>

State <sup>a</sup>	Configuration <sup>b</sup>	Excitation Energy (eV) <sup>c</sup>	
		<u>3s2p</u>	<u>4s3p</u>
X <sup>2</sup> A <sub>1</sub>	4b <sub>2</sub> <sup>2</sup> ba <sub>1</sub> 1b <sub>1</sub> <sup>2</sup> 1a <sub>2</sub> <sup>2</sup>	0.00	0.00
1 <sup>4</sup> A <sub>2</sub>	4b <sub>2</sub> <sup>2</sup> ba <sub>1</sub> 1b <sub>1</sub> <sup>2</sup> 1a <sub>2</sub> <sup>2</sup> 2b <sub>1</sub>	2.05	2.13
1 <sup>4</sup> B <sub>2</sub>	4b <sub>2</sub> <sup>2</sup> 6a <sub>1</sub> 1b <sub>1</sub> <sup>2</sup> 1a <sub>2</sub> <sup>2</sup> 2b <sub>1</sub>	2.10	2.14
1 <sup>2</sup> B <sub>1</sub>	4b <sub>2</sub> <sup>2</sup> 1b <sub>1</sub> <sup>2</sup> 1a <sub>2</sub> <sup>2</sup> 2b <sub>1</sub>	2.50	2.50
1 <sup>2</sup> A <sub>2</sub>	4b <sub>2</sub> <sup>2</sup> 6a <sub>1</sub> <sup>2</sup> 1b <sub>1</sub> <sup>2</sup> 1a <sub>2</sub>	2.80	2.83
1 <sup>2</sup> B <sub>2</sub>	4b <sub>2</sub> <sup>2</sup> 6a <sub>1</sub> <sup>2</sup> 1b <sub>1</sub> <sup>2</sup> 1a <sub>2</sub> <sup>2</sup>	3.82	3.84

<sup>a</sup> All states at bond length of 2.25 a.u. and bond angle of 134°

<sup>b</sup> The omitted orbitals 1a<sub>1</sub>, 1b<sub>2</sub>, 2a<sub>1</sub>, 3a<sub>1</sub>, 2b<sub>2</sub>, 4a<sub>1</sub>, 3b<sub>2</sub>, 5a<sub>1</sub> are doubly occupied in each configuration.

<sup>c</sup> The SCF total energy of the X <sup>2</sup>A<sub>1</sub> state is -203.95597 a.u. for the 4s3p basis set and -203.94646 a.u. for the 3s2p basis set. The difference in eV is 0.26.

TABLE VIII  
EXCITATION ENERGIES FOR NO<sub>2</sub>

State <sup>a</sup>	Configuration <sup>b</sup>	Excitation Energy (eV)	
		This Work <sup>c</sup>	Experiment <sup>d</sup>
X <sup>1</sup> A <sub>1</sub>	4b <sub>2</sub> <sup>2</sup> 6a <sub>1</sub> <sup>2</sup> 1b <sub>1</sub> <sup>2</sup> 1a <sub>2</sub> <sup>2</sup>	0.0	0.0
1 <sup>3</sup> B <sub>2</sub>	4b <sub>2</sub> <sup>2</sup> 6a <sub>1</sub> <sup>2</sup> 1b <sub>1</sub> <sup>2</sup> 1a <sub>2</sub> 2b <sub>1</sub>	2.30	-
1 <sup>1</sup> B <sub>2</sub>	4b <sub>2</sub> <sup>2</sup> 6a <sub>1</sub> <sup>2</sup> 1b <sub>1</sub> <sup>2</sup> 1a <sub>2</sub> 2b <sub>1</sub>	6.08	~6 <sup>e</sup>
1 <sup>3</sup> A <sub>1</sub>	4b <sub>2</sub> <sup>2</sup> 6a <sub>1</sub> <sup>2</sup> 1b <sub>1</sub> 1a <sub>2</sub> <sup>2</sup> 2b <sub>1</sub>	7.43	-

a) All states at bond length 2.40 bohr and bond angle of 116.8°

b) The omitted orbitals 1a<sub>1</sub> 1b<sub>2</sub> 2a<sub>1</sub> 3a<sub>1</sub> 2b<sub>2</sub> 4a<sub>1</sub> 3b<sub>2</sub> 5a<sub>1</sub> are doubly occupied in each configuration.

c) Vertical

d) Adiabatic

e) W. G. Trawick and W. H. Eberhardt, J. Chem. Phys. 22, 1402 (1954);  
R. M. Hochstrosser and A. P. Marchetti, J. Chem. Phys. 50, 1727 (1969);  
L. E. Harris H. S. Mar a, and S. P. McGlynn, Czech. J. Phys. B20,  
1007 (1970).



Via PUBLICATIONS PLANNED AND IN PREPARATION

1. Vertical Spectra for  $\text{CO}_2^-$  and Electron Affinity of  $\text{CO}_2$ . E. Sachs.
2. Application of the Differential Correlation Energy Method to the Calculation of the Electron Affinity of CN and  $\text{CO}_2$ . A. C. Wahl, E. Sachs, and J. Detrich.
3. A Review of Ab Initio Calculations on  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{N}_2\text{O}$ ,  $\text{O}_3$  and their Positive and Negative Ions. J. Detrich, E. Sachs, and A. C. Wahl.
4. Documentation of the Biggmoli and Pipano-Shavitt CI codes. F. Tobin, SAI-TR-80-232-03. (Internal document only).

VIB RECENT PUBLICATIONS IN TECHNICAL JOURNALS  
FROM THIS PROJECT

1. Theoretical Studies of Atmospheric Molecules: SCF and Correlated Energy Levels for the  $\text{NO}_2$ ,  $\text{NO}_2^+$ , and  $\text{NO}_2^-$  Systems  
P. J. Fortune, B. J. Rosenberg, W. B. England, and A. C. Wahl  
Theoret. Chem. Acta 46, 185(1977)
2. Ab Initio Calculations of the Minimum Energy Path in the Doublet Surface for the Reaction  $\text{N}(^4\text{S}) + \text{O}_2(^3\Sigma_g^-) \rightleftharpoons \text{NO}(^2\Pi_u) + \text{O}(^3\text{P})$   
P. Benioff, G. Das, and A. C. Wahl  
J. Chem. Phys. 67, 2449(1977).
3. Mechanisms of the Reaction of Ground State Positive Atomic Oxygen Ions with Nitrogen  
D. G. Hopper  
J. Amer. Chem. Soc. 100, 1019(1978).
4. Ab Initio Calculations of the Vertical Electronic Spectra of  $\text{NO}_2$ ,  $\text{NO}_2^+$  and  $\text{NO}_2^-$   
P. A. Benioff  
J. Chem. Phys. 68, 3405(1978).
5. Ab Initio Calculations on  $\text{NO}_2$  and  $\text{NO}_2^-$ : Optimization of Diffuse Gaussian Exponents  
P. A. Benioff, Theoret. Chem. Acta 00, 000(1978).
6. Theoretical Studies of Atmospheric Triatomic Molecules: New Ab Initio Results for the  $^1\Pi_g - ^1\Delta_u$  Vertical State Ordering in  $\text{CO}_2$   
W. B. England and W. C. Ermler,  
J. Chem. Phys. 70, 1711(1979).
7. An Improved MCSCF Method  
C. C. J. Roothaan, J. Detrich, and D. G. Hopper  
Int. J. Quantum Chem. 13 S(1979).
8. The Differential Correlation Energy Method for the Calculation of Electron Affinities, Ionization Potentials, and Electronic Spectra  
A. C. Wahl, E. S. Sachs, and J. H. Detrich  
Int. J. Quantum Chem. 14 S, 0000 (1980).
9. Theoretical Studies of Atmospheric Molecules  
J. H. Detrich, E. S. Sachs, and A. C. Wahl  
Int. J. Quantum Chem. 14 S, 0000 (1980).
10. A Practical Guide to Application of the MCSCF Method  
J. H. Detrich and A. C. Wahl  
NRCC-MCSCF Workshop Proceedings.  
National Resource for Computation in Chemistry, July, 1980.
11. General Quadratically Convergent MCSCF Theory in Terms of Reduced Matrix Elements  
C. C. J. Roothaan and J. H. Detrich  
Reviews of Modern Physics

## VII INTERACTIONS AND ATTENDANCE AT MEETINGS

- October 1978 - J. Detrich, Trip to Washington to discuss NBS contract and Wisconsin contract
- November 28 - December 1, 1979 - J. Detrich, APS Meeting, Division of Electron and Atomic Physics
- May 3 - 5, 1979 - J. Detrich, Midwest Theoretical Chemistry Conference (Poster Presentation)
- July 11 - 15, 1979 - J. Detrich, OSU Spectroscopy Conference 34th Symposium on Molecular Spectroscopy (2 talks)
- August 13 - 18, 1979 - J. Detrich, Gordon Conference on Few Body Interactions
- Summer 1979 - J. Detrich, Numerous discussions of new MCSCF method with scientists at NBS, NRCC, and the Gordon Conference
- September 17 & 18, 1979 - J. Detrich, DOD Physics Review - NAS Washington, D.C.
- March 9 - 15, 1980 - J. Detrich, Sanibel Symposium - Palmcoast, Florida
- May 10 & 11, 1980 - J. Detrich, Midwest Theoretical Chemistry Conference, Minneapolis Minnesota
- July 14 - 16, 1980 - J. Detrich, NRCC - MCSCF Workshop - College Station, Texas
- May 3 - 5, 1979 - A. C. Wahl, Midwest Theoretical Chemistry Conference, Chairman Session I
- June 1, 1979 - A. C. Wahl, Discussion of current and future status of AFOSR contract with R. Kelley, Physics Directorate AFOSR, Washington, D.C.
- September 17 & 18, 1979 - A. C. Wahl, DOD Physics Review, NAS Washington, D.C.
- November 5 & 6, 1979 - A. C. Wahl, DOD Chemistry Review, NAS Washington, D.C.
- March 9 - 15, 1980 - A. C. Wahl, Sanibel Symposium - Palmcoast, Florida
- May 10 & 11, 1980 - A. C. Wahl, Midwest Theoretical Chemistry Conference, Minneapolis, Minnesota
- June 20 - 25, 1980 - A. C. Wahl, Spectroscopy Conference - Columbus, Ohio
- July 14 - 16, 1980 - A. C. Wahl, NRCC - MCSCF Workshop - College Station, Texas
- July 21 - 25, 1980 - A. C. Wahl, Gordon Conference - Wolfeboro, New Hampshire

May 3 - 5, 1979 - E. Sachs, Midwest Theoretical Chemistry Conference,  
La Fayette, Indiana

July 25 - 27, 1979 - E. Sachs, Workshop on Software Standards and Computational  
Chemistry, Salt Lake City, Utah.

March 13 - 18, 1978 - D. Hopper, Sanibel Symporium - Palmcoast, Florida

March 18 - 20, 1978 - D. Hopper, Eleventh Midwest Theoretical Chemistry  
Conference, Columbus, Ohio

May 28 - June 2, 1978 - D. Hopper, Twenty-Sixth Annual Conference on Mass  
Spectrometry and Allied Topics, St. Louis, Missouri

June 12 - 16, 1978 - D. Hopper, Thirty-Third Annual Symposium on Molecular  
Spectrometry, Columbus, Ohio

March 11 - 17, 1979 - D. Hopper, Sanibel Symporium, Palmcoast, Florida

June 3 - 8, 1979 - D. Hopper, Twenty-Seventh Annual Conference on Mass  
Spectrometry and Allied Topics.

July 11 - 15, 1979 - D. Hopper, Thirty-Fourth Symporium on Molecular  
Spectroscopy, Columbus, Ohio.

Sept. 17 - 18, 1979 - D. Hopper, DOD Physics Review, Washington, D.C.

Oct. 29 - Nov. 3, 1979 - D. Hopper, Third International Conference of  
Quantum Chemistry, Kyoto, Japan.

Over the past year, A. C. Wahl has interacted by telephone and letter with  
a number of atmospheric scientists whose experimental work relates to this  
AFOSR contract (NBS, NOAA, JILA, SRI).

#### VIII PROJECT PERSONNEL

Below the names and durations of association with project of personnel is given:

J. Detrich joined the project in September 1978 and is presently associated with the project as project scientist.

D. G. Hopper joined the project in March 1978. His association with the project ended in November 1979.

Ed Sachs joined the project in June 1978 and left to accept a permanent position at Bell Labs in September 1979.

Frank Tobin joined the project in October 1978, left in June of 1979 and accepted a position at Johns Hopkins University.

Chris Wahl brought the project to SAI from Argonne beginning March of 1978, was on a leave of absence due to illness July 1978 through June 1979, and is currently principal investigator.

## IX Concluding Remarks

We believe that this comprehensive systematic project has enhanced our knowledge and understanding of the atmospheric triatomic systems under study. In many cases, particularly for excited states and ions, new information has been generated which was not and continues not to be available experimentally. In addition, during the course of this work several powerful methods for investigating molecular structure were developed.

It is our hope that the Air Force will continue to support this exciting work which can form the basis for improved modelling and for new insights into our understanding of the chemistry and physics of the earth's atmosphere.

#### X REFERENCES

1. AFOSR Proposal 1974, A. C. Wahl and G. Das.
2. AFOSR Proposal 1975, A. C. Wahl and G. Das.
3. AFOSR Proposal 1976, A. C. Wahl.
4. AFOSR Proposal 1977, A. C. Wahl.
5. AFOSR Proposal 1978, A. C. Wahl and D. Hopper.
6. A. C. Wahl and G. Das, Methods of Electronic Structure Theory, H. F. Schaefer III (ed.) (Vol. 3 of Modern Theoretical Chemistry, Plenum, New York, 1977), pp. 51-78.
7. C. C. J. Roothaan, J. Detrich, and D. G. Hopper, Int. J. Quantum Chem. S13, 93 (1979); C. C. J. Roothaan and J. Detrich, to be published in Revs. Mod. Phys.
8. T. H. Dunning, Jr., "Gaussian Basis Sets for Molecular Calculations," in Methods of Electronic Structure Theory, H. F. Schaefer III (ed.), (Vol. 3 of Modern Theoretical Chemistry, Plenum, New York, 1977), pp. 1-27.
9. P. J. Fortune, D. G. Hopper, B. J. Rosenberg, W. B. England, G. Das, A. C. Wahl and T. O. Tiernan, "Potential Energy Surface for Air Triatomics. Volume II. Results of SCF and Preliminary OVC Calculations," Aerospace Research Laboratory, USAF (ARL TR 75-0202, Vol. II, June, 1975).
10. A. C. Wahl, W. B. England, B. J. Rosenberg, D. G. Hopper, and P. J. Fortune, "Theoretical Studies of the Atmospheric Triatomic Molecules  $H_2O$ ,  $N_2O$ ,  $NO_2$ ,  $CO_2$ ,  $O_3$ , and Their Ions," Argonne National Laboratory (ANL-77-3, September 1976).
11. J. Pacansky, U. Wahlgren and P. S. Bagus, J. Chem. Phys. 62, (1975).
12. I. Suzuki, J. Mol. Spectry. 25, 479 (1968).
13. R. N. Compton, P. W. Reinhardt and C. D. Cooper, J. Chem. Phys. 63, 3821 (1975).
14. P. K. Pearson, H. F. Schaefer III, J. H. Richardson, L. M. Stephenson, and J. I. Brauman, J. Amer. Chem. Soc. 96, 6778 (1974).
15. P. A. Benioff, J. Chem. Phys. 68, 3405 (1978).

APPENDIX I  
PUBLICATIONS RESULTING FROM  
THE ATMOSPHERIC PROJECT

These publications report atmospheric related research performed with the support of the Air Force Office of Scientific Research, the Advanced Research Projects Agency, the Aerospace Research Laboratories, the Atomic Energy Commission, the Energy Research and Development Administration and the Department of Energy over the period 1972 - 1980.

The work represented by these papers involved a number of individual contracts involving A. C. Wahl and his collaborators, P. Benioff, G. Das, J. Detrich, W. England, P. Fortune, D. Hopper, R. Hosteny, B. Rosenberg, E. Sachs, W. Stevens, and C. W. Wilson.



## TECHNIQUE PAPERS

### Application of Perturbation Theory in Large Configuration Interaction Calculations

P. J. Fortune and B. J. Rosenberg  
Chem. Phys. Lett. 37, 110-114 (1977)

### A Modified Pseudopotential Approach to the Heavy-Atomic Molecular Systems: Application to the $X^2\Sigma_{1/2}^+$ , $A^2\Pi_{1/2}$ , and the $A^3\Pi_{3/2}$ States of the HgH Molecule

G. Das and A. C. Wahl  
J. Chem. Phys. 64, 4672-4679 (1976)

BISON-MC: A FORTRAN Computing System for MCSCF Calculation on Atoms, Diatoms and Polyatoms. This polyatomic MCSCF-CI capability was developed out of this project. This has been widely used in polyatomic MCSCF calculations by many researchers.

G. Das and A. C. Wahl, ANL-7955 (1972)

### An Improved MCSCF Method

C. C. J. Roothaan, J. Detrich, and D. G. Hopper, I.J.Q.C. S13, 93 (1979):  
C. C. J. Roothaan and J. Detrich, To be published.

### The Differential Correlation Energy Method for Electron Affinities, Ionization Potentials and Vertical Spectra

A. C. Wahl, E. Sachs, and J. H. Detrich, International Journal of Quantum Chemistry S14, 0000 (1980).

### Theoretical Studies of Atmospheric Triatomic Molecules

J. H. Detrich, E. Sachs, A. C. Wahl, International Journal of Quantum Chemistry S14, 0000 (1980).

## BOOK CHAPTERS

### A case History in Computer Resource Sharing: Ab Initio Calculations Via a Remote Control

D. G. Hopper, P. J. Fortune, A. C. Wahl and T. O. Tiernan  
COMPUTER NETWORKING AND CHEMISTRY, ACS SYMPOSIUM SERIES, Number 19,  
P. Lykos, Editor (American Chemical Society, Washington, 1975),  
pp 153-182

### The Multiconfiguration Self-Consistent Field Method

A. C. Wahl and G. Das  
METHODS IN ELECTRONIC STRUCTURE THEORY, H. F. Schaefer III, Editor  
(Plenum, New York, 1977), pp 51-78  
(37)

### WATER AND ITS IONS

MCSCF Calculations on the Lowest Triplet State of  $H_2O$

R. P. Hosteny, A. R. Hinds, A. C. Wahl, and M. Krauss  
Chem Phys. Lett. 23, 9-12 (1973)

Theoretical Studies of Atmospheric Molecules: SCF and Correlated Potential  
Surface Results for the  $X^2B_1$  and  $B^2B_2$  states of  $H_2O^+$

P. J. Fortune, B. J. Rosenberg, and A. C. Wahl  
J. Chem. Phys. 65, 2201-2205 (1976)

### OZONE AND ITS IONS

Recent applications of the Multiconfiguration Self-Consistent Field Method  
to Polarizabilities, Excited States, Van Der Waals Forces, and Triatomic  
Surfaces

A. Karo, M. Krauss, and A. C. Wahl  
Int. J. Quantum Chem. S7, 143-159 (1973)

Atmospheric Studies: Theoretical Study of the Ozone System ( $O_3$ )

A. C. Wahl and C. W. Wilson, Jr.  
Technical Report on ARPA Order No. 2022. (1972)

Vibrational Spectrum and Transition Intensities of Ozone

A. C. Wahl, P. Benioff, G. Das, and C. W. Wilson, Jr.  
Technical Report on AFOSR-ISSA-74-004, (1974)

### CARBON DIOXIDE AND ITS IONS

Ab Initio Vertical Spectra and Linear Bent Correlation Diagrams for the  
Valence States of  $CO_2$  and its Singly Charged Ions

W. B. England, B. J. Rosenberg, P. J. Fortune, and A. C. Wahl  
J. Chem. Phys. 65, 684-691 (1976)

Theoretical Studies of Atmospheric Triatomic Molecules: Accurate SCF  
Vertical Spectrum for Valence, Mixed Character, and Rydberg States of  
CO<sub>2</sub>

W. B. England, W. C. Ermler, and A. C. Wahl  
J. Chem. Phys. 66, 2336-2343 (1977)

Theoretical Studies of Atmospheric Triatomic Molecules: Ab Initio Equations-  
of-Motion Excitation Energies for Valence States of the Configuration  
 $1\pi^3g\ 2\pi^1u$  in CO<sub>2</sub>

W. B. England, D. Yeager, and A. C. Wahl  
J. Chem. Phys. 66, 2344-2345 (1977)

Theoretical Studies of Atmospheric Triatomic Molecules: New Ab Initio  
Results for the  $^1\Pi_g \rightarrow ^1\Delta_u$  Vertical Ordering in CO<sub>2</sub>

W. B. England and W. C. Ermler  
J. Chem. Phys. 70, 1711-1719 (1979)

#### NIOTROGEN DIOXIDE AND ITS IONS

The Electronic Structure of Nitrogen Dioxide. I. Multiconfiguration  
Self-Consistent-Field Calculation of the Low-Lying Electronic States

G. D. Gillispie, A. U. Khan, A. C. Wahl, R. P. Hosteny, and  
M. Krauss  
J. Chem. Phys. 63, 3425-3444 (1975)

Theoretical Studies of Atmospheric Molecules: SCF and Correlated Energy  
Levels for the NO<sub>2</sub>, NO<sub>2</sub><sup>+</sup> AND NO<sub>2</sub><sup>-</sup> Systems

P. J. Fortune, B. J. Rosenberg, W. B. England, and A. C. Wahl  
Theoret. Chem. Acta 46, 185 (1977)

Ab Initio Calculations of the Minimum Energy Path in the Doublet Surface  
for the Reaction  $N(^4S) + O_2(^3\Sigma_g^-) \rightarrow NO(^2\Pi) + O(^3P)$

J. A. Benioff, G. Das, and A. C. Wahl  
J. Chem. Phys. 67, 2449-2462 (1977)

Ab Initio Calculations of the Vertical Electronic Spectra of  $NO_2$ ,  $NO_2^+$  and  
 $NO_2^-$

P. A. Benioff  
J. Chem. Phys. 68, 3405-3412 (1978)

Ab Initio Calculations on  $NO_2$  and  $NO_2^-$ : Optimization of Diffuse Gaussian  
Exponents

P. A. Benioff  
Theoret. Chem. Acta. 48, 337 (1978)

#### NITROUS OXIDE AND ITS IONS

Ab Initio Study of  $N_2O^+$ . Angular Dependence of the  $1^4A''(^4\Pi)$  Potential

D. G. Hopper  
Chem. Phys. Lett. 31, 446-450 (1975)

Theoretical and Experimental Studies of the  $N_2O^+$  and  $N_2O$  Ground States  
Potential Energy Surfaces. Implications for the  $O^- + N_2 \rightarrow N_2O + e$   
and Other Processes

D. G. Hopper, A. C. Wahl, R. L. C. Wu, and T. O. Tiernan  
J. Chem. Phys. 55, 5474-5494 (1976)

Mechanisms of the Reaction of Positive Atomic Oxygen Ions with Nitrogen

D. G. Hopper  
J. Amer. Chem. Soc. 100, 1019-1029 (1978)

## OTHER MOLECULES

Ab Initio Calculations of the Barrier for Internal Rotation in Nitrous Acid

P. Benioff, G. Das, and A. C. Wahl  
J. Chem. Phys. 64, 710-717 (1976)

Theoretical Transition Dipole Moments and Lifetimes for the  $A^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$  System of  $\text{Na}_2$

W. J. Stevens, M. M. Hessel, P. J. Bertoncini and A. C. Wahl  
J. Chem. Phys. 66, 1477-1482 (1977)

Molecular Orbital Correlation Diagrams for  $\text{He}_2$ ,  $\text{He}_2^+$ ,  $\text{N}_2$ ,  $\text{N}_2^+$ ,  $\text{CO}$  and  $\text{CO}^+$ ,

W. C. Ermler, R. S. Mulliken and A. C. Wahl  
J. Chem. Phys. 66, 3031 (1977)

Excited Electronic States of  $\text{O}_2^-$

M. Krauss, D. Neumann, A. C. Wahl, G. Das and W. Zemke  
Phys. Rev. A, 7, 69 (1973)

Study of the Ground State Potential Curve and Dipole Moment of OH by the Method of Optimized Valence Configurations

W. J. Stevens, G. Das, A. C. Wahl, M. Krauss and D. Neumann  
J. Chem. Phys. 61, 3686 (1974)

Accurate Ab Initio Potential Curves for the  $X^2\Pi_g$ ,  $A^2\Pi_u$ ,  $a^4\Sigma_u^-$ , and  $^2\Sigma_u^-$  States of the  $\text{O}_2^-$  Ion

G. Das, A. C. Wahl, W. T. Zenke, W. C. Stwalley,  
J. Chem. Phys. 68, 4252 (1978)

RELATED DOCUMENTS\*

Potential Energy Surfaces for Air Triatomics. Volume I. Literature Review

M. Krauss, D. G. Hopper, P. J. Fortune, A. C. Wahl and T. O. Tiernan  
ARL (AFSC) TR75-0202, Vol. I, June 1975

Potential Energy Surfaces for Air Triatomics. Volume II. Results of SCF and Preliminary OVC Calculations

P. J. Fortune, D. G. Hopper, B. J. Rosenberg, W. B. England,  
G. Das, A. C. Wahl, and T. O. Tiernan  
ARL (AFSC) TR75-0202, Vol. II, June 1975

Theoretical Studies of Atmospheric Triatomic Molecules  $H_2O$ ,  $N_2O$ ,  $NO_2$ ,  $CO_2$ ,  $O_3$ , and Their Ions

A. C. Wahl, W. B. England, B. J. Rosenberg, D. G. Hopper, and  
P. J. Fortune  
Argonne National Laboratory Technical Report ANL-77-3, 1977

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